MECHANICAL PROPERTIES OF POLYMERS

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Summary

Mechanical and dynamic mechanical properties of various polymers over a wide range of experimental conditions are discussed in this chapter. Statistical molecular theory, large deformation theory, and finite element idealization are described, and their applicability to predicting the stress-strain curves of polymers are elucidated. Experimental stress-strain plots of elastomers, plastics, block co-polymers, and fibers indicate differences among the polymers. Stress-elongation versus stress-retraction curves and stress-strain plots under various deformations are also highlighted. After a detailed theoretical background on dynamic mechanical properties, zones of viscoelastic behavior and temperature and frequency effects are discussed. Dynamic mechanical spectra of glassy polymers, crystalline polymers, and elastomers are explained, and their
structure-property relationship is established. Ultimate properties of various polymers are also covered.

1. Introduction to Mechanical Properties: General Considerations

Polymers are usually described as viscoelastic materials, which emphasizes their intermediate position between viscous liquids and elastic solids. An ideal linear elastic solid obeys Hooke’s law, i.e. stress is proportional to strain. An ideal viscous liquid obeys Newton’s law, i.e. stress is proportional to the rate of change of strain. At low temperatures or high frequencies of measurement, a polymer may behave like a glass with a Young’s modulus of $10^9$ N/m$^2$ to $10^{10}$ N/m$^2$ and will break at strains greater than about 5%. At high temperatures or low frequencies, the same polymer may display rubber-like behavior with a low modulus of $10^6$ N/m$^2$ to $10^7$ N/m$^2$ and extension larger than 100% without any permanent set. At still higher temperatures, the polymer behaves like a highly viscous liquid. In the intermediate temperature or frequency range, the polymer is neither glassy nor rubber-like. It shows an intermediate modulus, is viscoelastic, and may dissipate a considerable amount of energy on being strained.

Mechanical properties of solid polymers have been discussed in terms of two approaches: (a) microscopic description of the particular facet of polymer behavior and (b) molecular description using chemical composition and physical structures. To the author’s mind, both approaches are important to understand the mechanical properties and hence this chapter will highlight these areas.

2. Deformation Behavior of Polymers

Figure 1 displays the load-elongation curves for a polymer at four different temperatures. At temperatures well below the glass transition temperature, brittle fracture occurs and the load rises to the breaking point at low strains. At high temperature (Curve D), the polymer is rubber-like, and the load rises to the breaking point at high strains with a sigmoidal relationship to the elongation. In the intermediate range (Curves B and C), a yield point before rupture is observed.
When a polymer is deformed, the stress increases with strain. Typical stress-strain curves in tension for selected polymers are given in Figure 2. The properties of these polymers can be related to the characteristics of their stress-strain curves. Tests may be performed in shear, flexure, compression, torsion, or tension. Typical high elasticity of rubber arises from its molecular structure. The polymer molecules are long, flexible, and coiled and take up random configurations under Brownian thermal motion. They are straightened out by deformation under an applied force. When the force is released, they spring back to random shapes as fast as their thermal motion allows.
Figure 2. Stress-strain curves of a few polymers

Elastic materials that are isotropic in their underformed state can be described by the fundamental elastic constants. The first deals with their resistance to compression in volume under a hydrostatic pressure. Bulk modulus, $K'$, is defined by the relation between the applied pressure $P$ and the consequent shrinkage $\Delta V$ of the original volume $V_0$.

$$P = K' \left( \frac{\Delta V}{V_0} \right)$$

(1)

The second constant describes the resistance to simple shearing stress $\sigma_{xy}$. Termed the shear modulus $G$, it is defined as

$$G = \sigma_{xy} / \gamma$$

(2)

where $\gamma$ is the amount of shear defined as the lateral displacement to the height of the sheared block.

The tensile or Young’s modulus, $E$, is defined as the ratio of a simple tensile stress $\sigma$ to the corresponding tensile strain, $\varepsilon$. 

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\[ E = \frac{\sigma}{\varepsilon} = \frac{9K'G}{3K' + G} \tag{3} \]

Poisson’s ratio \( \nu \) defined by the lateral contraction strain \( \varepsilon_2 \) to longitudinal tensile strain \( \varepsilon_1 \), for a bar subjected to a single tensile stress, is given by

\[ \nu = \frac{1}{2} \frac{3K' - 2G}{3K' + 2G} \tag{4} \]

Rubbery materials have high values of bulk modulus (1.5 GPa to 2 GPa), low shear modulus (0.5 MPa to 10 MPa), and a Poisson’s ratio of 0.4995. Hence, the tensile modulus, \( E \), can be approximated to \( 3G \), following Eq. (3).

The stresses can be resolved into nine components and the stress state can be described in terms of stress tensor as follows:

\[
\sigma_{ij} = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix}
\tag{5}
\]

where the first subscript gives the normal to the plane on which the stress acts and the second subscript defines the direction of the stress. The components \( \sigma_{11}, \sigma_{22}, \) and \( \sigma_{33} \) are known as the normal stresses.

It is often useful to divide the stress tensor into a hydrostatic or dilatational component, which causes a volume change, and into a deviatoric or pure shear component, which causes a change in shape. The hydrostatic component \( p \) of the stress tensor is given by

\[ p = \frac{1}{3} (\sigma_{11} + \sigma_{22} + \sigma_{33}) \tag{6} \]

And the deviatoric stress tensor \( \sigma'_{ij} \) is found by subtracting the hydrostatic stress from the overall tensor such that

\[
\sigma'_{ij} = \begin{bmatrix}
(\sigma_{11} - p) & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & (\sigma_{22} - p) & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & (\sigma_{33} - p)
\end{bmatrix}
\tag{7}
\]

The engineering strain, \( \varepsilon \), which is often used in the linear elastic analysis of polymers, is defined as

\[ \varepsilon = \delta l / l \tag{8} \]

The extension ratio, \( \lambda \), is used when large strains are encountered.
\[ \lambda = 1 + \frac{\delta l}{l} \quad (9) \]
\[ \lambda = 1 + \varepsilon \quad (10) \]

It is possible to describe the state of strain in terms of a strain tensor \( \varepsilon_{ij} \)

\[
\varepsilon_{ij} = \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}
\end{bmatrix}
\]

(11)

Often the terms plane stress and plane strain are used. Plane stress is obtained in deformed thin sheets. Another important situation arises when one of the three principal strains, \( \varepsilon_3 \), is equal to zero. This is a two-dimensional state of strain known as a plane strain.

The relationship between stress and strain in uniaxial tension or compression at low strain can be expressed by Hooke’s law. Polymers however, tend not to obey Hooke’s law (Figure 1). But this relationship can be used to define Young’s modulus, \( E \). For uniaxial tension or compression

\[ E = \frac{\text{Stress}}{\text{Strain}} \quad (12) \]

Typical values of Young’s modulus are given below for different types of polymers measured at room temperature and moderate testing rates.

<table>
<thead>
<tr>
<th>Type of polymer</th>
<th>Modulus, ( E ) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber</td>
<td>( \sim 10^6 )</td>
</tr>
<tr>
<td>Semicrystalline polymer (above ( T_g ))</td>
<td>( \sim 10^8 )</td>
</tr>
<tr>
<td>Semicrystalline polymer (below ( T_g ))</td>
<td>( \sim 10^9 )</td>
</tr>
<tr>
<td>Glassy polymer</td>
<td>( \sim 10^9 )</td>
</tr>
<tr>
<td>Semicrystalline polymer fiber</td>
<td>( \sim 10^{10} )</td>
</tr>
<tr>
<td>Polymer single crystal fiber</td>
<td>( \sim 10^{11} )</td>
</tr>
</tbody>
</table>

Table 1. Modulus of various polymers

Although the above relationship for stress and strain cannot be applied to complex systems, Hooke’s law can be generalized such that every stress component is a linear function of every strain component. For example,

\[ \sigma_{11} = A_{11} \cdot \varepsilon_{11} + A_{22} \cdot \varepsilon_{22} + A_{33} \cdot \varepsilon_{33} + \ldots \quad (13) \]

where \( A_s \) are the stiffness constants. In general,
\[ \sigma_{ij} = C_{ijkl} \varepsilon_{ij} \]  

(14)

where \( C_{ijkl} \) is a fourth rank tensor containing all stiffness constants.

The elastic constants \( E \) and \( \nu \) can be used to show how a body will respond to a set of principal stresses \( \sigma_{11}, \sigma_{22}, \text{and } \sigma_{33} \). A stress of \( \sigma_{11} \) will cause a strain of \( \sigma_{11} / E \) along the l direction, but will also lead to strains of \( -\nu \sigma_{11} / E \) along the 2 and 3 directions. Thus it follows that

\[
\varepsilon_{11} = \frac{\sigma_{11}}{E} - \frac{\nu}{E} \left( \sigma_{22} + \sigma_{33} \right)
\]

\[
\varepsilon_{22} = \frac{\sigma_{22}}{E} - \frac{\nu}{E} \left( \sigma_{33} + \sigma_{11} \right)
\]

\[
\varepsilon_{33} = \frac{\sigma_{33}}{E} - \frac{\nu}{E} \left( \sigma_{11} + \sigma_{22} \right)
\]

(15)

3. Statistical Molecular Theories

3.1. Single Polymer Chain

For a polymer chain with \( n \) links, each of which has a length \( l \), the fully extended length of the chain would be \( nl \). As this extended conformation is just one of the myriad conformations that the chain can assume, the number of conformations for a given separation of chain ends \( x \) may be given by the well-known Gaussian error function.

\[
w(x) = \left( \frac{3}{2} \pi n l^2 \right)^{1/2} \exp \left( -\frac{3x^2}{2 nl^2} \right)
\]

(16)

This can be written in the form of a continuous distribution function, \( w(x) \ dx \) representing the probability of finding a value of \( x \) between \( x \) and \( x + dx \) given as

\[
w(x) \ dx = \left( \frac{3}{2} \pi n l^2 \right)^{1/2} \left[ \exp \left( -\frac{3x^2}{2 nl^2} \right) \right] dx
\]

(17)

In three dimensions,

\[
w(x,y,z) \ dx \cdot dy \cdot dz = \left( \frac{b}{\pi^{1/2}} \right)^3 \left[ \exp \left( -\frac{b^2 r^2}{2 n l^2} \right) \right] dx \cdot dy \cdot dz
\]

(18)

where \( b^2 = \frac{3}{2} n l^2 \) and \( r^2 = x^2 + y^2 + z^2 \)

Eq. (18) gives the probability that if one end of a random chain is located at the origin of a Cartesian coordinate system, the other end can be found in the volume element \( dx\cdot dy\cdot dz \) at a distance \( r \) away (Figure 3). This can also be given by the radial distribution function,

\[
w(r) \ dr = \left( \frac{b}{\pi^{1/2}} \right)^3 \left[ \exp \left( -\frac{b^2 r^2}{2 n l^2} \right) \right] 4 \pi r^2 \ dr
\]

(19)
where $4 \pi r^2 \, dr$ is the volume element of a spherical shell of thickness $dr$ located at a distance $r$ from the origin.

Figure 3. Volume element $dx, dy, dz$ at a distance $r$ away from the origin

Long molecular chains can have many configurations of equal energy in response to the micro-Brownian motion of their constituent atoms. It may be assumed that the chains in rubber form a network in which the small number of links does not affect the motions of the chains. External forces constrain the arrangement of the chains and decrease the configurational entropy. An evaluation of the stress-strain relationship thus calculates the entropy of a single chain and then the change in entropy of the complete network of chains as a function of strain. The entropy of a single chain is related to the number of conformations through the Boltzmann relations

$$S = k \ln w \quad (20)$$

where $k$ is the Boltzmann constant.

From the first law of thermodynamics

$$dU = dQ - dW \quad (21)$$

where $U$ is the internal energy, $Q$ is heat, and $W$ is work. Assuming only work is the stress-strain work of the chain,

$$dW = -fdr \quad (22)$$

where $f$ is the elastic force.

Thus,
\[ dU = TdS + f dr \quad (23) \]

Transforming this to the Helmholtz free energy function \( A \),
\[ dA = dU - TdS \quad (24) \]

Or the force can be obtained
\[ f = \left( \frac{\partial A}{\partial r} \right)_T \quad (25) \]

It may be assumed that the internal energy is not affected by the conformational changes, and the Helmholtz function will be determined by the entropy term alone
\[ S = k \ln w \quad (26a) \]
\[ = c' - k \cdot b^2 \cdot r^2 \quad (26b) \]

Thus,
\[ A = A' + k \cdot T \cdot b^2 \cdot r^2 \quad (27) \]

where \( A' \) is that part of the free energy unaffected by conformations. Differentiating this with respect to \( r \)
\[ f = 2 \cdot k \cdot T \cdot b^2 \cdot r \quad (28) \]

Eq. (28) predicts that the elastic force of a chain is directly proportional to the end-to-end length of a chain, and a single random chain will obey Hooke’s law.

### 3.2. Polymer Network

For a polymer network of long chains, the Gaussian theory of rubber elasticity is formulated on the basis of the following assumption:

- The internal energy of the network is independent of deformation.
- The individual network chains can be described by Gaussian statistics.
- The free energy of the network is the sum of the free energies of the individual chains.
- The deformation is affine.

Thus,
\[ A_u = A' + kT \sum_{i=1}^{N} b^2 \left( x_i^2 + y_i^2 + z_i^2 \right) \quad (29) \]

\( A_u \) is the free energy of the undeformed network consisting of \( N \) chains.
In the deformed state

\[ A_d = A' + kT \sum_{i=1}^{N} b^2 \left( \lambda_i^2 x_i^2 + \lambda_i^2 y_i^2 + \lambda_i^2 z_i^2 \right) \]  

(30)

where \( \lambda_1, \lambda_2, \) and \( \lambda_3 \) are the deformation ratios in the \( x, y, \) and \( z \) directions. Since \( r^2 = x_i^2 + y_i^2 + z_i^2 \) for a random isotropic network,

\[ x_i^2 = y_i^2 = z_i^2 = \frac{r_i^2}{3} \]  

(31)

Therefore,

\[ \Delta A = \frac{1}{3} kT \sum_{i=1}^{N} b^2 r_i^2 \left( \lambda_i^2 + \lambda_i^2 + \lambda_i^2 - 3 \right) \]  

(32a)

\[ = \frac{1}{3} N kT \left\langle b^2 r^2 \right\rangle \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \]  

(32b)

Where

\[ \left\langle b^2 r^2 \right\rangle = \sum_{i=1}^{N} \frac{b^2 r_i^2}{N} \]

Because

\[ \sum_{i=1}^{N} \frac{r_i^2}{N} = \left\langle r_i^2 \right\rangle, \]

we have

\[ \left\langle b^2 r^2 \right\rangle = \frac{3}{2} \left\langle \frac{r_i^2}{r_o^2} \right\rangle \]  

(33)

\[ \Delta A = \frac{1}{2} N kT \left( \frac{\left\langle r_i^2 \right\rangle}{r_o^2} \right) \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right) \]  

(34)

under uniaxial extension

\[ \lambda_i = \frac{L}{L_0} = \lambda \]  

(35)

and assuming the volume is constant on deformation.
\( \lambda_1 \cdot \lambda_2 \cdot \lambda_3 = 1 \) \hspace{1cm} (36)

Hence,
\[
\lambda_2 = \lambda_3 = \frac{1}{\lambda^{1/2}}
\] \hspace{1cm} (37)

Eq. (34) now becomes
\[
\Delta A = \frac{1}{2} NK T \left( \frac{r_{1}^2}{r_{0}^2} \right) \left( \lambda^2 + \frac{2}{\lambda} - 3 \right)
\] \hspace{1cm} (38)

The work of deformation per unit volume
\[
W = \frac{1}{2} NK T \left( \frac{r_{1}^2}{r_{0}^2} \right) \left( \lambda^2 + \frac{2}{\lambda} - 3 \right)
\] \hspace{1cm} (39)

If \( f \) is the force per unit unstrained cross-sectional area,
\[
f = \left( \frac{\partial A}{\partial \lambda} \right)_{T,\gamma} = NK T \left( \frac{r_{1}^2}{r_{0}^2} \right) \left( \lambda - \frac{1}{\lambda^2} \right)
\] \hspace{1cm} (40)

Under uniaxial compression \( \lambda < 1 \), the same formula applies \( f \) being negative. The properties in either extension or compression are thus represented by a single continuous function.

For a large shear strain in the \((x\ y)\) plane, the principal axes of strain are defined by the extension ratios
\[
\lambda_1 = \lambda, \quad \lambda_2 = 1, \quad \lambda_3 = \frac{1}{\lambda}
\] \hspace{1cm} (41)

And the corresponding shear strain
\[
\gamma = \lambda - \frac{1}{\lambda}
\] \hspace{1cm} (42)

Hence,
\[
\Delta A = \frac{1}{2} NK T \left( \frac{r_{1}^2}{r_{0}^2} \right) \left( \lambda^2 - 2 + \frac{1}{\lambda^2} \right)
\] \hspace{1cm} (43a)
\[
\sigma_{xy} = \left( \frac{\partial \Delta A}{\partial \gamma} \right) = \frac{N k T \gamma}{A} \quad (44)
\]

The stress of an elastomer is linearly proportional to strain at low strains (Hookean). At higher strains, the behavior becomes nonlinear, referred to as Neo-Hookean behavior. The elastic force is directly proportional to absolute temperature and number of network chains. They are in accord with the experimental findings.

In formulating the Gaussian theory of rubber elasticity, it was necessary to assume that the internal energy of the elastomer remains unaffected by conformational changes. In real elastomers, the energetic contribution cannot be neglected. Many investigators have suggested that the energy contribution to the total force in natural rubber may be about 10% to 20% at room temperature.

\[
f = f^e + f^s \quad (45)
\]

\[
f^e = \text{energetic component} \quad f^s = \text{entropic component}
\]

\[
\frac{f^e}{f} = 1 - \frac{d \ln G}{d \ln T} - \frac{\beta T}{3} \quad (46)
\]

where \( \beta = \text{isobaric coefficient of thermal bulk expansion} \).

The Gaussian assumption limits the application of the model to relatively small extension. In the region of high strains, i.e. for \( r / n_l > 1/3 \) to 1/2, non-Gaussian statistics should be employed. The Gaussian assumption may be replaced by the Inverse Langevin approximation. The distribution function may be given by

\[
w(r) = C \exp \left\{ -n \left[ \frac{r L^1(\frac{r}{n_l})}{n_l} \right] + \ln \left[ \frac{L^1(\frac{r}{n_l})}{\text{Sinh} L^1(\frac{r}{n_l})} \right] \right\} \quad (47)
\]

and

\[
f = \frac{N_0 k T}{3} n^{1/2} \left[ L^1 \left( \frac{\lambda}{n_l^{1/2}} \right) - \lambda^{3/2} L^1 \left( \frac{1}{\lambda^{1/2} n_l^{1/2}} \right) \right] \quad (48)
\]
For small values of $\lambda$, this equation reduces to the Gaussian expression. This method predicts a large increase in tensile stress at high extensions, i.e. sigmoidal stress-strain curve typical of elastomers such as natural rubber. From time to time researchers have come out with new models to explain the nonlinear nature of the stress-strain curve.

Bibliography


Biographical Sketch

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